Mobility of imidacloprid from alginate-bentonite controlled-release formulations in greenhouse soils

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Abstract: The mobility of imidacloprid [1-(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine] from alginate-based controlled-release (CR) formulations was investigated in two different soil profiles. In one, a layered bed system simulating the typical arrangement under a plastic greenhouse, which is composed of sand, peat, amended soil and native soil, was used. In the other, the layer containing amended soil was used in order to determine the mobility of the insecticide in a soil system with a low content of organic matter and a high content of clay. Two CR formulations based on sodium alginate (1.87% wt/wt), imidacloprid (1.21%), natural or acid-treated bentonite (3.28%), and water (93.64%) were compared to technical grade imidacloprid. The use of alginate CR formulations produced less vertical mobility of the active ingredient as compared to the technical product. With the technical grade product treatment, the total amount of imidacloprid leached from columns packed with amended soil was 82.3% of that applied, whereas for the alginate-based CR formulations containing natural or acid-treated bentonite, the leached percentages were 44.7% and 37.1%, respectively. In the column experiments simulating the layered bed system, no insecticide was found in the leachate when the alginate-based CR formulations containing natural bentonite were used. However, 3% of the applied imidacloprid appeared when the treatment was carried out with technical grade material. Sorption-desorption capacities of the various soil layers for imidacloprid molecules were also calculated using batch experiments.

Keywords: imidacloprid; leaching; controlled release; bentonite; soil

1 INTRODUCTION

Imidacloprid [1-(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine] is a systemic insecticide with a novel mode of action.[1,2] This insecticide is effective for controlling aphids, whiteflies, thrips, scales, psyllids, plant bugs and various other harmful pest species, including resistant strains. It is used as seed-dressing, soil treatment, and foliar treatment in different crops.[3] This insecticide is widely applied in the region of Almería, in Andalucía (south-eastern Spain), where intensive horticulture is practised. This is based on a raised layered bed system under plastic greenhouses irrigated from underground aquifers. There is concern that the aquifers supplying irrigation water are becoming depleted and that these are becoming contaminated with pesticides.[4–6] The pollution of groundwater with pesticides is effected through run-off, leaching and improper application. Several pest-control strategies have been reported in an effort to reduce the amount of pesticide used, such as biological control systems, integrated pest management and controlled-release (CR) formulations. The latter can regulate (and often slow) the rate of availability of a pesticide, localizing it in the crop zone and reducing the amount accessible to leaching.[7] Fernández-Pérez *et al*[8] investigated the controlled release of imidacloprid from a pine kraft lignin matrix, using both a flow-through system and soil columns. The authors reported that the use of controlled-release lignin matrixes clearly reduced the vertical mobility of imidacloprid into the soil layer columns.

The use of columns composed of uniform layers of the various soil constituents of the layered bed system (ie native soil, amended soil, peat and sand) to assess leaching processes in the greenhouse is considered valid, as each of the layers in the greenhouses is disturbed and mixed as much as those in a laboratory layered soil column. Preliminary use of such columns combined with an appropriate leaching model supported this view.[9]

In a previous paper related to the study here presented, González-Pradas *et al*[10] described a series

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Table 1. Characteristics of the four layers of greenhouse soil

Layer	pH	Organic matter (%)	Clay content (%)	Field capacity (% v/v)	Water saturation (% v/v)	CEC (meq 100 g^{-1})
Sand	9.39	0.02	–	5.80	40	10.00
Peat	3.28	81.32	–	77.0	128	116.25
Amended soil	8.44	0.08	53.00	38.0	52	10.63
Native soil	8.87	0.51	8.00	48.0	51	12.50

of alginate-based imidacloprid CR formulations. In a water-release study, the authors reported that the use of natural and acid-treated bentonites as modifying agents of the basic formulation (sodium alginate-imidacloprid-water) reduced the release rate of the insecticide as compared with technical imidacloprid and with alginate formulation without sorbents. The objective of the present study was to evaluate the potential of alginate-bentonite CR formulations to reduce leaching of imidacloprid. Therefore, the mobility of imidacloprid from two alginate-based CR formulations containing bentonite was compared to that of technical grade material using soil columns.

2 MATERIALS AND METHODS

2.1 Soil characterization

The soils used were a calcareous soil (Camborthids) and an amended soil (Xerosol-Luvic), from the Almería region. A commercial peat was used as the organic matter layer (Hydro del Báltico, Navasa S A). The sand was obtained from an unused commercial greenhouse. The individual layers of the soil from the greenhouse were characterized in terms of their physical properties. Air-dried samples, less than 2 mm particle size, were analysed by standard methods. The pH was determined in a 1:2.5 soil/water suspension using a glass electrode;[11] organic matter content was determined by the Walkley–Black method;[12] clay content was determined by the hydrometer method;[13] cation exchange capacity was determined by the barium acetate method[14] and water saturation and field capacity were determined following the guidelines by Hall *et al*.[15] All these characteristics are shown in Table 1.

2.2 Sorption-desorption studies

The sorption experiments were carried out as follows: aqueous calcium chloride solutions (0.01 M) containing initial imidacloprid concentrations (C_0) between 1.45 and 31.23 mg litre^{-1} were used. Aqueous suspensions of the samples were prepared by adding 25 ml of each imidacloprid solution to 3.0 g of native soil, amended soil or sand, or 0.5 g of peat. These were placed in stoppered conical flasks and shaken for 24 h (the time required for equilibrium to be reached between imidacloprid sorbed and imidacloprid in solution) in a shaker bath at 25 ($\pm$0.1) °C. After shaking, the solutions were centrifuged at 9250 *g* for 10 min and the concentration of imidacloprid in the supernatant liquid was determined by high performance liquid chromatography (HPLC). The HPLC operating conditions were as follows: separation by isocratic elution was performed on a 150 × 3.9 mm Nova-Pack LC-18 bonded-phase column (Waters, Millipore Corporation); sample volume, 20 µl; flow rate, 1.0 ml min^{-1}; mobile phase: acetonitrile + water (65 + 35 by volume). Imidacloprid was analysed at 269 nm, its wavelength of maximum absorption. External standard calibration was used. The imidacloprid sorbed was calculated from the difference between the initial and the final solution concentrations. Blanks containing no imidacloprid and three replicates of each sorption point were used for each series of experiments.

Desorption experiments were carried out by adding aqueous calcium chloride solution (0.01 M; 25 ml) to the stoppered conical flasks containing the higher initial pesticide concentration (C_0 = 31.23 mg litre^{-1}), after removal of the sorption supernatant. This system was again shaken for a 24-h period to establish the new equilibrium. This treatment was also followed by centrifugation and determination of the new equilibrium concentration in the supernatant. The amount of imidacloprid desorbed in the first equilibration was calculated. This process was repeated four times. Blanks containing no imidacloprid were used for each case, and all desorption experiments were carried out in triplicate.

2.3 Controlled release formulations

Imidacloprid technical grade (99.0%) was provided by Bayer Hispania Industrial, Spain. A natural bentonite (98% montmorillonite, containing sodium as exchange ion), previously described by González-Pradas *et al*,[16] was used as modifying agent in alginate-based CR formulations, and also for the preparation of the acid-treated bentonite sample. Acid activation of the bentonite was carried out in boiling sulfuric acid (0.5 mole) for 1 h, and the resulting sample was heated at 105 °C to constant weight. Chemical composition and textural properties of the sample were also previously studied by the present authors.[17] The product so obtained, and the natural bentonite are referred to as B-0.5 and B respectively.

Controlled-release formulations were obtained by using a method similar to that described by González-Pradas *et al*.[10] These formulations contained sodium alginate (1.87% wt/wt) from Sigma Chemical, St Louis, MO, B or B-0.5 (3.2%), and technical grade

imidacloprid (1.21%). Technical grade imidacloprid was first dissolved in water. Alginate and B or B-0.5 were gradually added, and the slurry was vigorously stirred for 1 h to obtain homogeneous mixtures. The alginate mixtures were added dropwise to a 300-ml gellant bath of 0.25 M calcium chloride using the apparatus described by Connick.[18] The resulting beads were allowed to gel in the 0.25 M calcium chloride solution for a total of 5 min, then they were filtered and allowed to dry, first at room temperature and then in an oven (40 °C) to constant weight. The two products so obtained are referred to as IAB (dry CR granules prepared with the B sample) and IAB-0.5 (dry CR granules prepared with the B-0.5 sample). The IAB and IAB-0.5 formulations contained 108.9 g AI kg^{-1}, and 123.1 g AI kg^{-1}, respectively.

2.4 Mobility experiments

Mobility of technical and formulated imidacloprid was compared in two different soil profiles. One of them, simulating the typical arrangement of the different layers in a greenhouse, was composed of sand, peat, amended and native soil, and the other one simulated a general situation of a soil system with a low content of organic matter and a high content of clay. In the latter study, the soil used was a Xerosol-Luvic, widely used in greenhouses as amended soil, and representative of a large area of south-eastern Spain.

2.4.1 Column preparation

Columns packed with greenhouse soil layers were prepared by splitting a poly(vinyl chloride) (PVC) pipe (7 cm ID., 60 cm long) longitudinally and applying 2-mm thick silicone ridges around the inside of the column at 5-cm increments to minimize boundary flow.[19] The two parts of each column were then put together and sealed with waterproof adhesive paste. Nylon mesh with an effective pore diameter of 60 μm and lined with a layer of fibreglass wool was sealed to the bottom of each column to prevent displacement of the soil from the columns and to minimize the dead-end volume.[20] Each column contained, from the bottom to the top, native soil (20 cm), amended soil (20 cm), peat (2 cm) and sand (10 cm). The different layers of the soil, screened through a 2-mm sieve, were added to the column in small increments to minimize the effect of particle size, obtaining the following final bulk densities: 1.17 (native soil), 1.43 (amended soil), 0.26 (peat), and 1.56 g cm^{-3} (sand).

A similar procedure was followed for the preparation of columns packed with amended soil. In this case, the columns used were shorter (26 cm long), and contained from the bottom to the top a layer of acid-washed sand (1 cm) and amended soil (20 cm).

Previous to the application of the insecticide, the columns were saturated with distilled water via capillarity and then left to drain for 24 hours.

2.4.2 Application of insecticide to the soil columns

The insecticide treatments were applied at a rate of 6.5 kg AI ha^{-1}. This rate was required to achieve adequate surface coverage.

All insecticide treatments (technical grade product and alginate-based CR formulations) were applied to duplicate soil columns. Technical grade imidacloprid was applied as follows: a methanol solution containing 10 mg of imidacloprid was added to 50 g (0.5 cm) of washed sand. The washed sand/insecticide mixture was left to dry overnight at room temperature before being added to the top of each column. After application of the herbicide, an additional 0.5 cm of washed sand was added to the top of the column. The alginate-based CR formulations (IAB and IAB-0.5) were evenly distributed on the washed sand layer.

2.4.3 Leaching and leachate collection

The leaching solution used in all experiments was 0.01 M calcium chloride. This was done to simulate the soil solution and to prevent dispersion of the soil during the leaching procedure.[21] Solution (1.5 litre, equivalent to that applied in greenhouses for one growth season) was leached at a flow rate of 8 ml h^{-1} using a Gilson Minipuls 3 Peristaltic Pump. The time and volume of each leachate were recorded. Aliquots were taken from the leachate, passed through 0.5-μm PTFE filters, and injected directly in the HPLC system. At the end of the leaching procedure, the columns were allowed to drain for 48 h.

2.4.4 Column analysis

The columns simulating the typical arrangement of the layers in a greenhouse were split vertically, and the soil was removed, obtaining four fractions corresponding to the native soil, amended soil, peat, and sand. In addition, for the native soil and amended soil, a partition was made into two 10-cm portions labelled as (1) and (2) representing the upper and lower fractions, respectively. For the columns packed with amended soil, the soil was removed in 5-cm increments. All fractions were dried at room temperature and homogenized. Sub-samples were extracted in conical flasks, placed in a shaker bath for 24 h with HPLC grade methanol (25 ml), filtered through Whatman No 42 paper, and analysed by HPLC, as described above.

3 RESULTS AND DISCUSSION

3.1 Sorption-desorption studies

To evaluate the sorption capacities of the different layers of the soil columns for imidacloprid, the experimental data points were fitted to the Freundlich equation.[22] The linear form of this equation is:

$$\log X = \log K_f + n_f \log C \qquad (1)$$

where X is the amount of insecticide sorbed (mg kg^{-1} sorbent), C is the equilibrium solution concentration (mg $litre^{-1}$) and K_f and n_f are constants that characterize the sorption capacity for the insecticide. The constant K_f is the amount of pesticide sorbed for

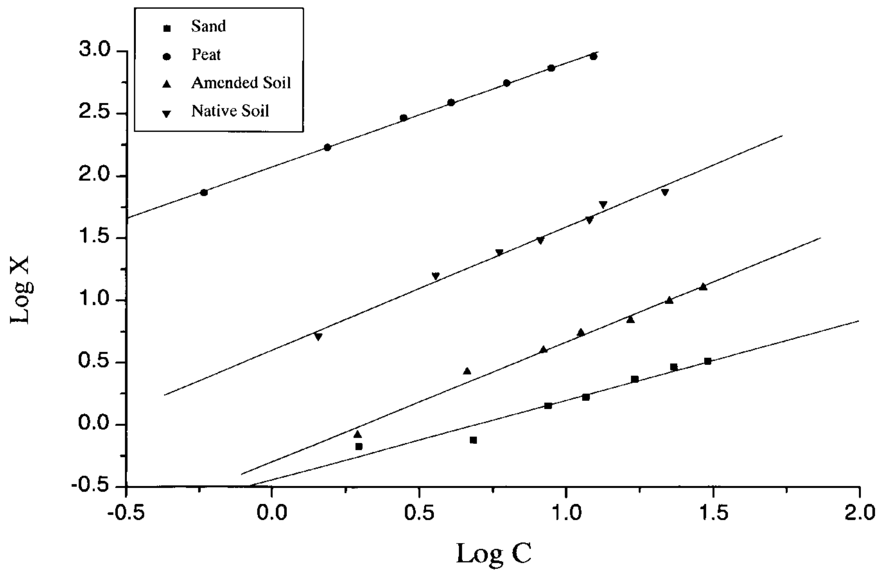

Figure 1. Application of Freundlich equation to adsorption of imidacloprid on different layers of a greenhouse soil.

Table 2. Parameters of Freundlich equation and correlation coefficients

Sample	K_f *(mg kg^{-1}) (± SEM)*	n_f *(± SEM)*	*r*
Sand	0.37 (±0.05)	0.63 (±0.05)	0.991[a]
Peat	121.0 (±14.2)	0.83 (±0.05)	0.999[a]
Amended soil	0.51 (±0.07)	0.96 (±0.04)	0.992[a]
Native soil	4.04 (±0.23)	0.97 (±0.04)	0.996[a]

[a] Significant at the 0.001 probability level.

an equilibrium concentration of 1 mg litre^{-1} and n is a measure of the intensity of adsorption and reflects the degree to which adsorption is a function of the concentration.[23] Figure 1 shows the fit of the experimental data points to Freundlich equation. The K_f and n_f values were calculated from the least-squares method applied to the linear form of the Freundlich equation and their values are summarized in Table 2. As can be seen from this table, the K_f values increase from 0.37 mg kg^{-1} for the sand to 121.0 mg kg^{-1} for the peat sample, the order being:

$$\text{sand} < \text{amended soil} < \text{native soil} \ll \text{peat}$$

The accumulated percentage of desorbed imidacloprid from the different sorbents, after four desorption cycles, is presented in Fig 2. These values range between 55.9% for the peat sample to 100% for the sand. For these experiments, the variation order is in

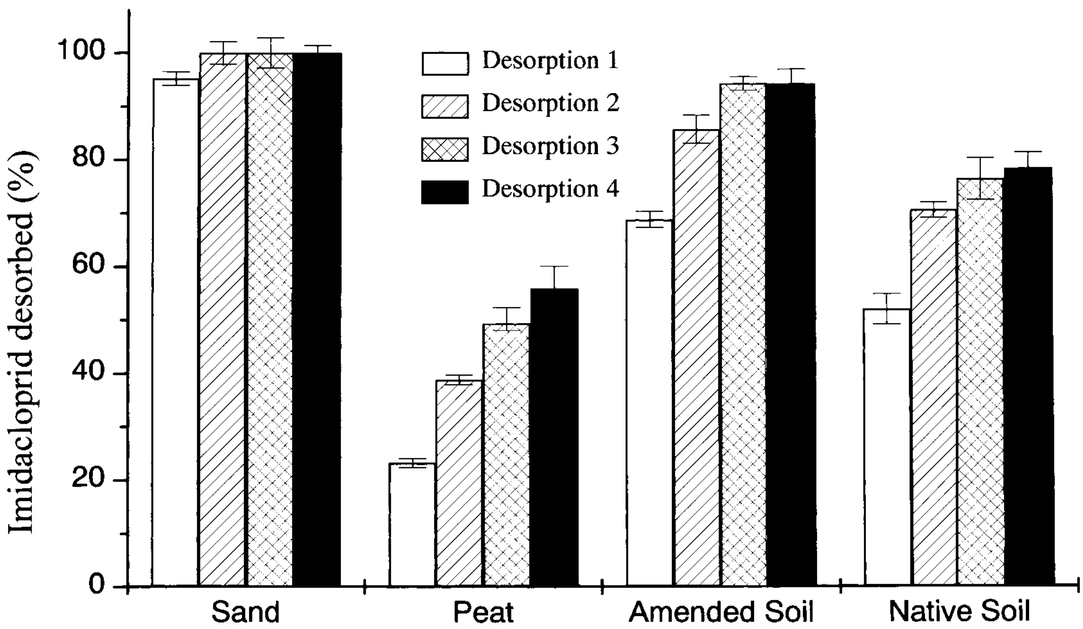

Figure 2. Cumulative imidacloprid desorbed from different layers of a greenhouse soil (error bars represent the standard deviation of three replicates).

Table 3. Imidacloprid extracted from amended soil segments and total percentages recovered from granules, soil and leachates

	Imidacloprid ($mg\,kg^{-1}$) ($\pm$SD)		
Depth (cm)	Technical grade material	IAB	IAB-0.5
0–5	0.07 ($\pm$0.01)	1.24 ($\pm$0.04)	0.33 ($\pm$0.05)
5–10	0.33 ($\pm$0.06)	0.22 ($\pm$0.07)	0.11 ($\pm$0.04)
10–15	1.35 ($\pm$0.09)	0.47 ($\pm$0.08)	0.18 ($\pm$0.03)
15–20	1.02 ($\pm$0.10)	0.69 ($\pm$0.06)	0.25 ($\pm$0.07)
Imidacloprid recovered (% of applied)			
in soil	7.8	7.4	2.5
in leachate	82.3	44.7	37.1
in granules	–	46.6	59.8

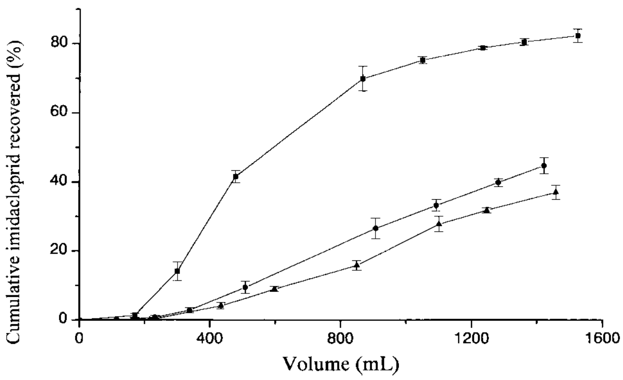

Figure 3. Cumulative imidacloprid leached from (■) technical grade material, (●) IAB, and (▲) IAB-0.5 in amended soil (error bars represent the standard deviation of three replicates).

general, inversely related to that obtained for the K_f values.

3.2 Mobility of imidacloprid in columns packed with amended soil

The amount of imidacloprid recovered per kilogram in each portion of the columns is presented in Table 3. In addition, the total percentages of imidacloprid recovered in the soil, leachate and granules relative to the total amount of insecticide applied in the experiments are also indicated in Table 3.

As can be seen, 7.8% of the insecticide is recovered from the soil when imidacloprid is applied as technical grade product, while 82.3% of the total amount applied is present in the leachate. The presence of this high amount of imidacloprid in the leachate was expected from (i) its relatively high solubility in water ($0.51\,g\,litre^{-1}$ at 20 °C) and the low value of K_{ow} (3.7), which indicates a potential capacity for mobility in soil, and (ii) the low value of K_f obtained from the sorption isotherm of imidacloprid for this soil. When imidacloprid was applied as alginate-based CR formulations (IAB and IAB-0.5), the amount of active ingredient recovered in the leachates was less than that obtained in columns treated with technical grade product (44.7% for the treatment with IAB granules and 37.1% for the columns treated with IAB-0.5 granules).

The characteristics of release of imidacloprid from alginate-based CR formulations in soil under dynamic conditions are related to those obtained in water under static conditions;[10] that is, the release of imidacloprid from the alginate-based CR formulation IAB-0.5 (39.6% in eight days) is slower than that observed for the alginate-based CR formulation IAB (52.1% in eight days). In addition, the release of imidacloprid from IAB and IAB-0.5 granules in the soil is much slower than that observed in water. The time taken for

Table 4. Imidacloprid extracted from greenhouse soil layers and total percentages recovered from granules, soil and leachates

	Imidacloprid recovered ($mg\,kg^{-1}$) ($\pm$SD)	
Layer	Technical grade material	IAB
Sand	1.22 ($\pm$0.11)	0.60 ($\pm$0.10)
Peat	92.50 ($\pm$1.17)	95.00 ($\pm$1.42)
Amended Soil (1)[a]	0.38 ($\pm$0.09)	0.53 ($\pm$0.07)
Amended Soil (2)[a]	0.42 ($\pm$0.07)	0.49 ($\pm$0.08)
Native Soil (1)[a]	12.29 ($\pm$0.64)	13.09 ($\pm$0.12)
Native Soil (2)[a]	2.33 ($\pm$0.12)	0.18 ($\pm$0.05)
Imidacloprid recovered (% of applied)		
in soil	89.3	86.8
in leachate	2.9	–
in granules	–	10.5

[a] (1) and (2) represent the upper and lower fractions in amended soil and native soil.

40% of the active ingredient to be released from alginate-based CR formulation IAB-0.5 in water under static conditions was 13 h, and the time taken for 52% of the active ingredient to be released from IAB granules in water was 17 h.[10] This fact might be explained if we consider that an occlusion of the formulation surface by soil particles takes place, as well as a slower diffusion within the soil as compared to water.[24,25] Soil water solutes may also retard movement of pesticides into the aqueous phase.[26,27]

The total recovery of imidacloprid at eight days from the soil columns treated with alginate-based CR formulation was 98.7% of the total applied for IAB treatment and 99.4% for the IAB-0.5 treatment. In both cases, the recovery was higher than that obtained with technical grade product which corresponds to 90.1% of the total applied. The granules recovered from the soil did not show any signs of disintegration or major degradation at the end of the experiment. The integrity of the CR granule is an important feature of non-erodible controlled-release formulations, as unpredictable fracture formation and breakage would increase the release surface of the matrix and thus the amount of active ingredient released.

The cumulative imidacloprid leached from soil columns treated with technical grade imidacloprid and alginate-based CR formulations (IAB and IAB-0.5) is shown in Fig 3. Significant differences were noted in the leaching patterns of the formulations investigated. The ranking of the formulations investigated in terms of percentage leached was as follows:

$$\text{IAB-0.5 (37.1\%)} < \text{IAB (44.7\%)} \ll \text{Technical grade product (82.3\%)}$$

For the technical grade product, imidacloprid was first detected in the leachate at approximately 0.17 litre. The amount of leached imidacloprid increased steadily over time to approximately 82% of the total applied by the termination of the experiment. For the alginate-based formulations IAB and IAB-0.5, imidacloprid was detected later in the leachate (0.23 litre for IAB and 0.43 litre for IAB-0.5). The amount leached from IAB formulation increased to 45% of that applied by the termination of the leaching procedure. Imidacloprid present in the IAB-0.5 formulation was leached to a smaller extent, with a total amount leached of 37%. It can be appreciated (Fig 3) that the use of alginate-based CR formulations reduces leaching of imidacloprid to a very acceptable level during the major part of the experiment compared to the technical grade product.

3.3 Mobility of imidacloprid in column packed with greenhouse soil layers

The amount of imidacloprid recovered in each portion of the columns is presented in Table 4. In addition, the total percentages of imidacloprid recovered in the soil, leachate and granules relative to the total amount of insecticide applied in the experiments are also given.

As can be seen, 89.3% of the total amount is recovered in the soil when imidacloprid is applied as technical grade product, and 2.9% of the total imidacloprid is present in the leachate. No imidacloprid was found in the leachate when this insecticide was applied as the IAB alginate-based formulation. Under these experimental conditions, slight differences were observed in the distribution patterns of imidacloprid between the technical product and IAB granules, although it is interesting to note that the amount of imidacloprid found in the deeper layer of the soil columns (native soil (2)) was less in the soil column treated with IAB granules ($0.18\,\text{mg kg}^{-1}$) than in the column treated with technical grade imidacloprid ($2.33\,\text{mg kg}^{-1}$). It can also be observed that the amount of imidacloprid recovered is higher for the peat layer than for the rest of the soil layers, which is in agreement with the values obtained for the K_f parameter and also with the observed desorption characteristics.

As can be deduced from the above, the use of alginate-bentonite CR formulation clearly reduces the vertical mobility of imidacloprid into the greenhouse soil layer columns, the peat showing the highest sorptive capacity under both static and dynamic conditions. From these results, it could be inferred that the use of formulations such as those described in this paper could reduce the possibility of imidacloprid reaching and contaminating groundwater resources, and they are especially indicated for the general working conditions used under plastic greenhouses.

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